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01/09/01



TRANSLATION FROM JAPANESE

(19) JAPANESE PATENT OFFICE (JP)  
(11) Japanese Laid-Open Patent Application (Kokai) No. 63-99228  
(12) Official Gazette for Laid-Open Patent Applications (A)

(51) Int. Cl.<sup>4</sup>: Classification Symbols: Internal Office Registration Nos.:  
C 08 G 63/76 NLL 7142-4J

(43) Laying-Open Date: April 30, 1988  
Request for Examination: Not yet submitted  
Number of Inventions: 1  
(Total of 12 pages [in original])

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(54) Title of the Invention: A Method for Manufacturing a Polyester Having a High Degree of Polymerization

(21) Application No. 62-15940  
(22) Filing Date: January 28, 1987  
Claim of Priority Right: (32) June 23, 1986 (33) Japan (JP) (31) Japanese Patent Application 61-144950  
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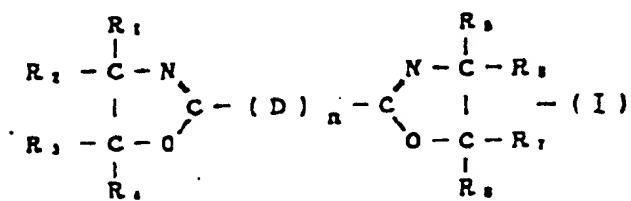
## SPECIFICATION

### 1. Title of the Invention

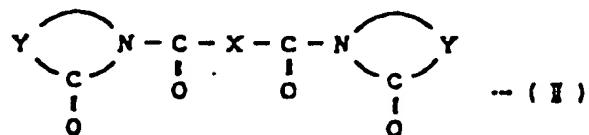
A Method for Manufacturing a Polyester Having a High Degree of Polymerization

### 2. Claims

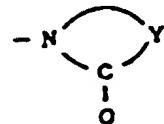
(1) A method for manufacturing a polyester having a high degree of polymerization, which is characterized by allowing an essentially linear saturated polyester to react in a molten state with at least one of the bisoxazoline compounds represented by General Formula I below



(in the formula, R<sub>1</sub> through R<sub>8</sub>, which may be the same or different, are hydrogen atoms or monovalent organic groups, D is a divalent organic group, and n is 0 or 1) and at least one of the bislactam compounds represented by General Formula II below

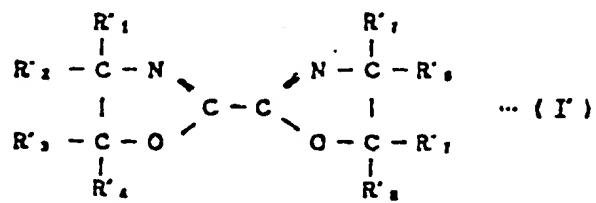


(in the formula, X and Y are divalent organic groups, and the cyclic structure



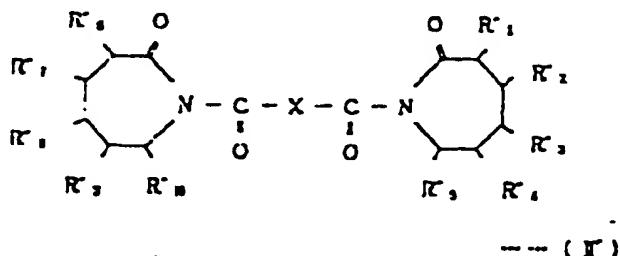
is a five- to seven-member ring), or with the reaction product of the aforementioned bisoxazoline compound and bislactam compound.

(2) The method according to Claim 1 for manufacturing a polyester having a high degree of polymerization, wherein the bisoxazoline compounds are those represented by General Formula I' below



(in the formula, R'\_1 through R'\_8, which may be the same or different, are hydrogen atoms or monovalent organic groups).

(3) The method according to Claim 1 for manufacturing a polyester having a high degree of polymerization, wherein the bislactam compounds are those represented by General Formula II' below



(in the formula, R'\_1 through R'\_10, which may be the same or different, are hydrogen atoms or monovalent organic groups, and X is a divalent organic group).

(4) The method according to Claim 1 or 2 for manufacturing a polyester having a high degree of polymerization, wherein the bisoxazoline compound is used in an amount of 0.1 to 10 wt% of the saturated polyester.

(5) The method according to Claim 1 or 3 for manufacturing a polyester having a high degree of polymerization, wherein the bislactam compound is used in an amount of 0.1 to 10 wt% of the saturated polyester.

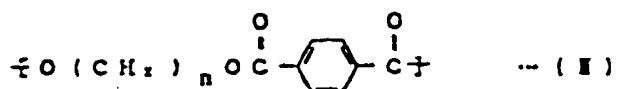
(6) The method according to Claim 1 for manufacturing a polyester having a high degree of polymerization, wherein the reaction product is obtained by allowing the

\* Translator's note: Some of the small subscripts and superscripts may be transcribed incorrectly owing to the poor legibility of the original.

bisoxazoline compound (BO) and the bislactam compound (BL) to react in a molar ratio (BO/BL) of 0.5 to 2.0.

(7) The method according to Claim 1 or 6 for manufacturing a polyester having a high degree of polymerization, wherein the reaction product is used in an amount of 0.1 to 10 wt% of the saturated polyester.

(8) The method according to Claim 1, 4, 5, or 7 for manufacturing a polyester having a high degree of polymerization, wherein the saturated polyester is one whose principal structural units are the repeating units represented by General Formula III below



(in the formula,  $n$  is 2 or 4).

### 3. Detailed Description of the Invention

## Field of Industrial Utilization

The present invention concerns a method for manufacturing a polyester having a high degree of polymerization, and, in particular, concerns a method for manufacturing a polyester having a high degree of polymerization and containing only a small amount of terminal carboxyl groups.

## Prior Art

Saturated linear polyesters, and, in particular, polyalkylene terephthalates such as polyethylene terephthalates, have many remarkable characteristics, and are therefore widely used as base materials for industrial fibers, films, and other moldings. There is, however, demand for higher strength and better hydrolysis resistance or heat resistance. Raising the degree of polymerization is an effective measure for imparting high strength to a polyester, and enhancing hydrolysis resistance or heat resistance is an effective means for reducing the amount of the terminal carboxyl groups contained in a polyester.

The methods proposed in Japanese Laid-Open Patent Applications 55-145734 and 55-161823 have recently attracted attention as the manufacturing methods that can

yield polyesters having high degrees of polymerization and containing only small amounts of terminal carboxyl groups.

These methods involve reacting a polyester and a bisoxazoline compound in a molten state, so a polyester containing only a small amount of terminal carboxyl groups and having a high degree of polymerization (occasionally referred to below as "a low-carboxyl-group, high-polymeric polyester") can be easily obtained because of the fact that the bisoxazoline compound simultaneously acts as a chain extender that raises the degree of polymerization of the polyester and as a carboxyl group depleting agent that lowers the amount of the terminal carboxyl groups contained in the polyester.

The disadvantage of a low-carboxyl-group, high-polymeric polyester thus obtained, however, is that the degree of polymerization decreases at a high rate when the polyester is kept in a molten state.

This is the reason that a polyester molding having a high degree of polymerization is difficult to obtain when the residence time during melt molding is considerable, and that even when the residence time is short and a polyester molding having a high degree of polymerization is obtained, moldability is still adversely affected by the smallest fluctuations in the residence time and in other molding conditions, bringing about noticeable deterioration in moldability (for example, a tendency for frequent yarn breakage during melt spinning).

To overcome this shortcoming, it has been proposed in Japanese Laid-Open Patent Applications 60-161427 and 60-163921 to use bisoxazoline compounds together with various other compounds, such as quaternary phosphonium salt compounds, tertiary phosphine compounds, or quaternary ammonium salt compounds. It is proposed in Japanese Laid-Open Patent Application 60-23583 to use reaction products of bisoxazoline compounds and dicarboxylic acid compounds.

All the resulting low-carboxyl-group, high-polymeric polyesters, however, are still characterized by a precipitous reduction in the degree of polymerization in the molten state, and are unsatisfactory in terms of thermal stability.

#### Objective of the Invention

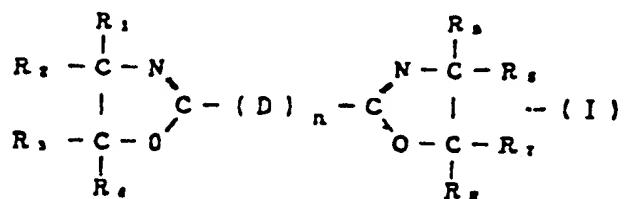
The objective of the present invention is to offer a method for manufacturing a polyester with a high degree of polymerization which is a low-carboxyl-group, high-

polymeric polyester obtained by the reaction between a polyester and a bisoxazoline compound, which is thermally stable in a molten state, and which is unaffected by the fluctuations in the melt molding conditions.

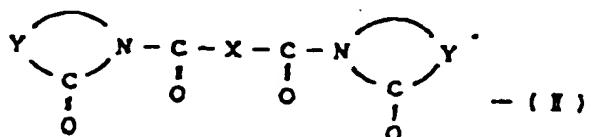
### Structure of the Invention

As a result of research aimed at attaining the stated objective, the inventors perfected the present invention after discovering that a reaction between a polyester and a bisoxazoline compound, on the one hand, and a bislactam compound, on the other hand, can yield a low-carboxyl-group, high-polymeric polyester which has a high degree of polymerization and in which the thermal stability in the molten state is substantially increased over that for a low-carboxyl-group, high-polymeric polyester obtained by a reaction involving the bisoxazoline compound alone.

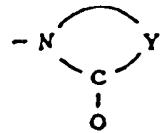
Specifically, the present invention concerns a method for manufacturing a polyester having a high degree of polymerization which is characterized by allowing an essentially linear saturated polyester to react in a molten state with at least one of the bisoxazoline compounds represented by General Formula I below



(in the formula, R<sub>1</sub> through R<sub>6</sub>, which may be the same or different, are hydrogen atoms or monovalent organic groups, D is a divalent organic group, and n is 0 or 1) and at least one of the bislactam compounds represented by General Formula II below



(in the formula, X and Y are divalent organic groups, and the cyclic structure



is a five- to seven-member ring), or with the reaction product of the aforementioned bisoxazoline compound and bislactam compound.

Examples of the acid components that constitute the saturated polyesters referred to in the present invention include terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, diphenyl dicarboxylic acid, diphenyl sulfone dicarboxylic acid, diphenoxymethane dicarboxylic acid, diphenyl ether dicarboxylic acid, methyl terephthalic acid, methyl isophthalic acid, and other aromatic dicarboxylic acids; succinic acid, adipic acid, sebacic acid, decane dicarboxylic acid, cyclohexane dicarboxylic acid, and other alicyclic dicarboxylic acids; and  $\epsilon$ -oxycaproic acid, oxybenzoic acid, hydroxyethoxybenzoic acid, and other oxycarboxylic acids, of which aromatic dicarboxylic acids are particularly suitable. In addition, examples of the glycol components used when the acid components are dicarboxylic acids include ethylene glycol, trimethylene glycol, tetramethylene glycol, hexamethylene glycol, decamethylene glycol, and cyclohexane dimethanol, of which ethylene glycol and tetramethylene glycol are particularly suitable.

It is also possible to use polyoxyalkylene glycols for some alcohol components; examples include polyoxyethylene glycol, polyoxytetramethylene glycol, and copolymers thereof. When a polyoxyalkylene glycol is used, its average molecular weight should be 500 to 5000, preferably 600 to 4000, and ideally 800 to 3000. The amount copolymerized should be 5 to 85 wt%, preferably 10 to 80 wt%, and ideally about 15 to 75 wt%, of the polyester. These copolymerization polyesters should be block copolymers.

Tri- and higher-functional compounds (such as trimethylol propane, pentaerythritol, trimellitic acid, and pyromellitic acid) or monofunctional compounds (such as benzoyl benzoic acid and diphenyl carboxylic acid) may be copolymerized with the aforementioned saturated polyesters as long as [the product] is essentially linear (for example, no more than 1 mol% with respect to the total acid component).

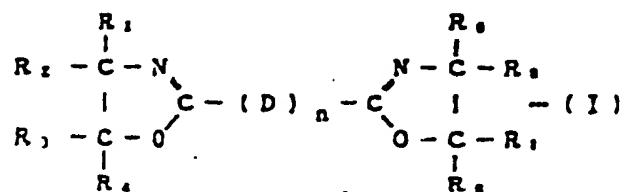
Any method may be used to manufacture such a polyester. The most common manufacturing method used, for example, in the case of polyethylene terephthalate

involves two reactions: a first-stage reaction in which terephthalic acid and ethylene glycol are allowed to undergo a direct ester reaction, or dimethyl terephthalate and ethylene glycol are allowed to undergo an ester-interchange reaction, to obtain a glycol ester of terephthalic acid and/or a low polymerization thereof; and a second-stage reaction in which the reaction composition obtained in the first stage is heated at a reduced pressure, the glycol formed is distilled off, and polymerization is performed. The degree of polymerization and the terminal carboxyl group content vary with the degree of polymerization and the terminal carboxyl group content of the desired polyester product, and thus cannot be unconditionally defined, but the degree of polymerization (in terms of intrinsic viscosity) is usually 0.4 or higher, and preferably 0.5 to 0.8, and the content of terminal carboxyl groups is usually 5 to 150 equivalents per  $10^6$  grams of polymer, and preferably 15 to 100 equivalents per  $10^6$  grams of polymer.

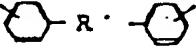
The desired catalyst can be used as needed in the first- and second-stage reactions, and additives (for example, colorants, delusterants, stabilizers, flame retardants, antistatic agents, and dyeing accelerators) may be admixed as needed.

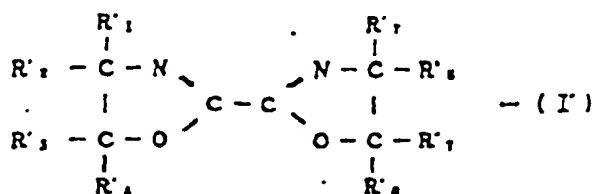
It is an important requirement of the present invention that the linear saturated polyester thus obtained be allowed to react in a molten state with a bisoxazoline compound and a bislactam compound, or with a reaction product of a bisoxazoline compound and a bislactam compound.

The bisoxazoline compound used in the present invention is represented by General Formula I below.



In General Formula I,  $R_1$  through  $R_8$  are each hydrogen atoms or monovalent organic groups; suitable examples of such monovalent organic groups include  $C_1$  to  $C_{10}$  alkyl groups,  $C_6$  to  $C_{12}$  aryl groups,  $C_5$  to  $C_{12}$  cycloalkyl groups, and  $C_8$  to  $C_{20}$  aralkyl groups.  $R_1$  through  $R_8$  may be the same or different; of these,  $R_1$  through  $R_5$  should all be hydrogen atoms. In the formula, D is a divalent organic group, for example, a  $C_1$  to  $C_{10}$  alkylene group, a  $C_6$  to  $C_{12}$  arylene group, a  $C_5$  to  $C_{12}$  cycloalkylene group, or a

$C_8$  to  $C_{20}$  aralkylene group. Specific examples of alkylene groups include methylene, ethylene, propylene, butylene, pentylene, hexamethylene, octamethylene, nonamethylene, decamethylene, and dimethyl methylene. Specific examples of arylene groups include phenylene, naphthylene, diphenylene,  (in the formula,  $R'$  is  $-O-$ ,  $-CO-$ ,  $-S-$ ,  $-SO_2-$ ,  $-CH_2-$ ,  $-C(CH_3)_2-$ , or the like). Specific examples of cycloalkylene groups include cyclooxylene groups. In the formula,  $n$  is 0 or 1; a compound represented by General Formula I' below (in which  $n$  is zero) is particularly suitable because it has an excellent chain extender effect.



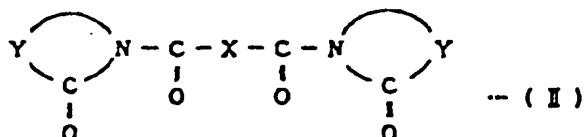
(in the formula,  $R'_1$  through  $R'_8$ , which may be the same or different, are hydrogen atoms or monovalent organic groups).

Specific examples of the bisoxazoline compounds represented by General Formula I above include 2,2'-bis(2-oxazoline), 2,2'-bis(4-methyl-2-oxazoline), 2,2'-bis(4,4'-dimethyl-2-oxazoline), 2,2'-bis(4-ethyl-2-oxazoline), 2,2'-bis(4,4'-diethyl-2-oxazoline), 2,2'-bis(4-propyl-2-oxazoline), 2,2'-bis(4-butyl-2-oxazoline), 2,2'-bis(4-hexyl-2-oxazoline), 2,2'-bis(4-phenyl-2-oxazoline), 2,2'-bis(4-cyclohexyl-2-oxazoline), 2,2'-bis(4-benzyl-2-oxazoline), 2,2'-*o*-phenylene bis(2-oxazoline), 2,2'-*m*-phenylene bis(2-oxazoline), 2,2'-*o*-phenylene bis(2-oxazoline), 2,2'-*p*-phenylene bis(4-methyl-2-oxazoline), 2,2'-*p*-phenylene bis(4,4-dimethyl-2-oxazoline), 2,2'-*m*-phenylene bis(4-methyl-2-oxazoline), 2,2'-*m*-phenylene bis(4,4-dimethyl-2-oxazoline), 2,2'-ethylene bis(2-oxazoline), 2,2'-tetramethylene bis(2-oxazoline), 2,2'-hexamethylene bis(2-oxazoline), 2,2'-octamethylene bis(2-oxazoline), 2,2'-decamethylene bis(2-oxazoline), 2,2'-ethylene bis(4-methyl-2-oxazoline), 2,2'-tetramethylene bis(4,4-dimethyl-2-oxazoline), 2,2'-9,9'-diphenoxoethane bis(2-oxazoline), 2,2'-cyclohexylene bis(2-oxazoline), and 2,2'-diphenylene bis(2-oxazoline). Of these, 2,2'-bis(2-oxazoline) yields the best results. These bisoxazoline compounds may be used individually or as combinations of two or more compounds.

A bisoxazoline compound should be used in an amount of 0.1 to 10 wt% with respect to the polyester. When the amount is less than 0.1 wt%, it is more difficult to

obtain a low-carboxyl-group, high-polymeric polyester, and when the amount exceeds 10 wt%, the effect by which the amount of the terminal carboxyl groups contained in the resulting polyester is reduced tends to reach saturation, as do other effects. It is even better for the amount used to be 0.2 to 5 wt%, and preferably 0.3 to 3 wt%.

The bislactam compound used in the present invention is the compound that is represented by General Formula II below.



(in the formula, X and Y are divalent organic groups, and the cyclic structure

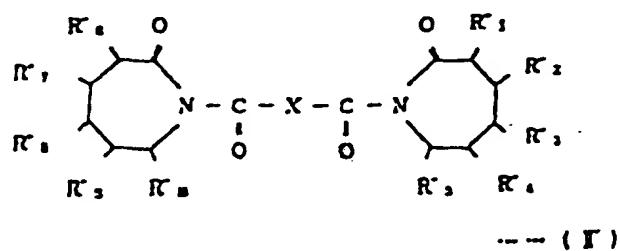


is a five- to seven-member ring).

As will be described in the practical examples below, such a bislactam compound, even when used alone, acts as a chain extender that increases the degree of polymerization without reducing the amount of the terminal carboxyl groups contained in the resulting polyester.

It is therefore assumed that the chain extending action of the bislactam compound is due to the coupling of the end OH groups of the polyester.

A compound represented by General Formula II' below should be used as such a bislactam compound.



(in the formula,  $R'_1$  through  $R'_{10}$ , which may be the same or different, are hydrogen atoms or monovalent organic groups, and  $X$  is a divalent organic group).

Specific examples of the aforementioned suitable bislactam compounds include *N,N'*-terephthalyl biscaprolactam, *N,N'*-isophthalyl biscaprolactam, *N,N'*-adipyl biscaprolactam, *N,N'*-adipyl bisvalerolactam, *N,N'*-isophthalyl butyrolactum, and *N,N'*-terephthalyl bisbutyrolactum. Of these, *N,N'*-terephthalyl biscaprolactam and *N,N'*-adipyl biscaprolactam are particularly suitable. These bislactam compounds may be used individually or as combinations of two or more compounds.

The bislactam compound employed in the present invention should be used in an amount of 0.1 to 10 wt% with respect to the polyester. When the amount is less than 0.1 wt%, the effects by which thermal stability is enhanced and the degree of polymerization is increased in a molten state tend to diminish, and when the amount exceeds 10 wt%, the aforementioned effects tend to reach saturation.

Such a bislactam compound may be mixed with a bisoxazoline compound and added to the polyester, or it may be admixed in advance into the polyester.

In such a case, the degree of polymerization and the thermal stability of the resulting polyester tend to be inadequate when the bislactam compound is added after the reaction between the polyester and the bislactam compound has been virtually completed.

The reaction between a bisoxazoline compound and a bislactam compound should be performed in advance in order to allow the polyester to safely react with the bisoxazoline compound and the bislactam compound.

Figure 1 shows an example of an infrared absorption spectrum (occasionally referred to below as "an IR spectrum") produced by the reaction product of a bisoxazoline compound and a bislactam compound.

Figure 1 shows the infrared absorption spectrum of a solid obtained by dissolving 2,2'-bis(2-oxazoline) (occasionally referred to below as "CE") and *N,N'*-terephthalbislactam (occasionally referred to below as "TL") in a molar ratio of 1:1 in methylene chloride, allowing the ingredients to react at room temperature while agitating them for 30 minutes, and then removing the methyl chloride by evaporation. Figures 2 and 3 show the infrared absorption spectra of 2,2'-bis(2-oxazoline) and *N,N'*-terephthalbislactam, respectively.

A comparison between the IR spectrum shown in Figure 1 and the IR spectra shown in Figures 2 and 3 shows that the absorption peak absent in the IR spectra of CE and TL in Figures 2 and 3 is visible near a wavelength of  $1720\text{ cm}^{-1}$  in the IR spectra shown in Figure 1, that the characteristic absorption peak near  $1720\text{ cm}^{-1}$  in the IR spectra of CE in Figure 2 has shifted to near  $1725\text{ cm}^{-1}$  in the IR spectrum shown in Figure 1, and that the characteristic absorption peak near  $1670\text{ cm}^{-1}$  in the IR spectrum shown in Figure 3 has shifted to near  $1680\text{ cm}^{-1}$  in the IR spectrum shown in Figure 1.

The melting point of the CE compound, the TL compound, and the solid (A) for which the IR spectrum in Figure 1 had been measured were determined by differential scanning calorimetry (DSC), and it was found that [the melting point of A] was lower than that of either CE or TL, as shown in the table below.

	Melting point
Solid A	$171^\circ\text{C}$
CE	214
TL	202

These results indicate that the solid 4 obtained by agitating CE and TL in methylene chloride at room temperature for 30 minutes and removing the methylene chloride by evaporation is the reaction product of CE and TL; as will be described below, [the product] reacts with the polyester, making it possible to obtain a low-carboxyl-group, high-polymeric polyester having a satisfactory thermal stability that equals or surpasses that attained when CE and TL are used in the form of a mixture. This suggests that the solid A may be a reaction adduct of CE and CL.

Bisoxazoline compounds and bislactam compounds can thus readily react in a solvent at room temperature.

In addition to methylene chloride, any compound capable of dissolving bisoxazoline compounds and bislactam compounds can be used as such a solvent. It is, for example, possible to use methanol, ethanol, or chloroform.

During the reaction between a bisoxazoline compound and a bislactam compound, the molar ratio (BO/BL) of the bisoxazoline compound (BO) and the bislactam compound (BL) should be 0.5 to 2.0.

In this case, when the BO/BL ratio is lower than 0.5, the effect by which the bisoxazoline compound reduces the amount of the carboxyl groups in the polyester tends to be less pronounced, and when the BO/Bl ratio exceeds 2.0, the effect by which the bislactam compound renders the polyester thermally stable tends to be less pronounced.

To ensure the optimum reduction in the carboxylation of the resulting polyester and the optimum increase in its degree of polymerization, the reaction product thus obtained should be used in an amount of 0.1 to 10 wt% with respect to the polyester.

Japanese Laid-Open Patent Application 55-164218 describes a method in which a polyester having a high degree of polymerization is manufactured by allowing a polyester to react with a chain extender (such as a bisoxazoline compound and a bislactam compound) capable of coupling the end OH groups of the polyester.

As will be described in Comparative Example 2 below, however, the polyester obtained by such a manufacturing method still lacks thermal stability in a molten state despite having a high degree of polymerization.

The present invention involves reacting a polyester in a molten state with a bisoxazoline compound and a bislactam compound or with a mixture of the bisoxazoline compound and the bislactam compound. The corresponding reaction temperature should lie between the melting point of the polyester and 320°C, and preferably between the melting point of the polyester and 290°C. The reaction may be conducted at an elevated pressure, but normal or reduced pressure is preferred. The reaction time should be 30 seconds to 60 minutes, and preferably 1 minute to 15 minutes. It is evident that the reaction can be performed by a method in which the two components are mixed and reacted under agitation in an ordinary polyester polymerization reactor. It is possible, for example, to react the two components by mixing them in an extruder, thus raising the degree of polymerization. The mixing can, for example, be conducted during slivering, film formation, or the injection molding of plastics.

The present invention allows a heat stabilizer (such as a hindered phenol-based compound) commonly used to improve the heat resistance of polyesters to be present during the reaction of the polyester with the bisoxazoline compound and the bislactam compound, or with the reaction product of the bisoxazoline compound and the

bislactam compound, or to be added to the polyester after the reaction has been completed.

#### Effect of the Invention

The present invention makes it possible to obtain a low-carboxyl-group, high-polymeric polyester whose degree of polymerization and whose thermal stability in a molten state are improved considerably over those of a conventional low-carboxyl-group, high-polymeric polyester obtained by the reaction between a polyester and a bisoxazoline compound.

The exact reason that such a low-carboxyl-group, high-polymeric polyester is obtained is not yet known, although it is assumed that a bisoxazoline compound and a bislactam compound act differently as chain extenders.

Specifically, the bisoxazoline compound selectively couples the terminal carboxyl groups of the polyester while the bislactam compound selectively couples the end OH groups of the polyester.

This is the reason that a polyester obtained by the reaction between a polyester and the aforementioned two compounds has a high degree of polymerization, a lower content of terminal carboxyl groups and end OH groups, and a better thermal stability than a conventional low-carboxyl-group, high-polymeric polyester obtained by a reaction involving a bisoxazoline compound alone, with the result that molding can be conducted stably and without being affected by the fluctuations in the melt molding conditions (when such fluctuations occur), and that the incidence of yarn breakage during melt spinning can be markedly reduced.

#### Merits of the Invention

The low-carboxyl-group, high-polymeric polyester obtained in accordance with the present invention can be used to advantage in the polyester fibers, films, plastic molded materials, and other polyester moldings for which a high degree of polymerization and a low content of carboxyl groups are required.

#### Practical Examples

The present invention will now be described in detail through practical examples.

### Practical Example 1

Bisoxazoline compounds and/or bislactam compounds (the types of compounds and the amounts in which they were added are shown in Table 1) were blended together, and the resulting mixtures were subsequently melt-extruded using an extruder at a temperature of about 300°C; the residence time for each case is shown in Table 1. (The amounts were calculated per 100 weight parts of a polyethylene terephthalate with an intrinsic viscosity ( $\eta$ ) of 0.80 and a terminal carboxyl group (COOH) content of 18 equivalents per 10<sup>6</sup> grams of polymer). Table 1 also shows the intrinsic viscosity ( $\eta$ ) and the terminal carboxyl group (COOH) content of the resulting extruded polymer.

In Table 1, Nos. 1 and 3 are practical examples of the present invention; each of the polyesters has a high degree of polymerization and satisfactory thermal stability.

By contrast, No. 4 is an example in which a bisoxazoline compound alone was allowed to react with a polyester, and the degree of polymerization and the thermal stability of the resulting polyester are much lower than those of polyester No. 1 or 3.

In addition, No. 2 is an example in which a bislactam compound alone was allowed to react with a polyester, and the resulting polyester, while having a somewhat better thermal stability than polyester No. 4, is still inferior to polyesters No. 1 and 3 in terms of degree of polymerization and thermal stability.

### Comparative Example 1

The intrinsic viscosity was measured for a polymer extruded from an extruder in the same manner as in Practical Example 1, except that the type of bisoxazoline compound or bislactam compound and/or the amount in which it was added (see No. 1 in Table 1 pertaining to Practical Example 1) was changed in the manner shown in Table 2. The measurement results are also shown in Table 2.

### Comparative Example 2

0.3 weight part of 2,2'-bis(2-oxazoline) and 0.3 weight part of 2,2'-*p*-phenylene bis(3,1-benzoxazin-4-one) were blended together per 100 weight parts of a polyethylene terephthalate with an intrinsic viscosity ( $\eta$ ) of 0.80 and a terminal carboxyl group (COOH) content of 18 equivalents per 10<sup>6</sup> grams of polymer, and the

resulting mixtures were subsequently melt-extruded using an extruder at a temperature of about 300°C; the residence time for each case is shown in Table 3.

Table 3 also shows the intrinsic viscosity ( $\eta$ ) and the terminal carboxyl group (COOH) content of the resulting extruded polymer.

The resulting polyester had a degree of polymerization comparable to that obtained in Practical Example 1, but its thermal stability in a molten state was lower.

### Practical Example 2

Bisoxazoline compounds and bislactam compounds were admixed into a polyester (the types of compounds and the amounts in which they were added correspond to Nos. 1 and 4 in Table 1 pertaining to Practical Example 1); and the molten admixture was subsequently discharged at 310°C, cooled, allowed to solidify, and then taken up at 2500 m/min.

The corresponding ratios of yarn breakage during spinning was 1.5% for No. 1 and 3.7% for No. 4.

During melt spinning, it was impossible to make the flowing state of the molten polymer into a perfect piston flow, nor was it possible to completely eliminate fluctuations in the residence time.

This is the reason that the polymer possessed inferior thermal stability (the same as polymer No. 4), the degree of polymerization decreased in the polymer portion characterized by a substantial residence time, and the aforementioned discharged portion that had a low degree of polymerization was apt to break up, causing numerous spun yarn breakages.

By contrast, with the polymer whose thermal stability was increased in the same manner as that of polymer No. 1, fluctuations in the residence time during spinning did not lower the degree of polymerization of the polymer to a level at which the spun yarn broke up, making it possible to reduce the frequency of spun yarn breakage.

### Practical Example 3

Reaction products of bisoxazoline compounds (BO) and bislactam compounds (BL) (the types of compounds are shown in Table 4) were each added in an amount of

1.0 weight part per 100 weight parts of a polyethylene terephthalate with an intrinsic viscosity ( $\eta$ ) of 0.80 and a terminal carboxyl group (COOH) content of 18 equivalents per  $10^6$  grams of polymer and melt-extruded using an extruder at a temperature of about 300°C; the residence time for each case is shown in Table 4. Table 4 also shows the intrinsic viscosity ( $\eta$ ) and the terminal carboxyl group (COOH) content of the resulting extruded polymer.

The reaction products of BO and BL shown in Table 4 were obtained by melting the two components in a molar ratio (BO/BL) of 1 in methylene chloride, allowing the components to react under agitation at room temperature for 30 minutes, and then removing the methylene chloride by evaporation.

As can be seen in Table 4, polyester Nos. 1 through 3 (which fall within the scope of the present invention) each have a high degree of polymerization and a satisfactory thermal stability.

Figure 1 shows the IR spectrum of the reaction product used in Section 1 of Table 1.

#### 4. Brief Description of the Figures

Figure 1 shows an infrared absorption spectrum of a solid obtained by dissolving 2,2'-bis(2-oxazoline) and *N,N'*-terephthalbislactam in a molar ratio of 1:1 in methylene chloride, allowing the components to react under agitation at room temperature for 30 minutes, and then removing the methylene chloride by evaporation. Figures 2 and 3 are infrared absorption spectra of 2,2'-bis(2-oxazoline) and *N,N'*-terephthalbislactam, respectively.

Table 1

No.	Bisoxazoline compound		Bislactam compound		Properties of extruded polymer													
	Name of compound	Amount added (wt%)	Name of compound	Amount added (wt%)	Residence time 5 min	10 min	15 min	20 min	30 min	(COOH)	( $\eta$ )							
1	2,2'-bis (2-oxazoline)	0.3	<i>N,N</i> -terephthal biscaprolactam	0.3	1.06	6	1.06	7	1.04	16	1.00	13	0.96	78				
2*	—	—	Same as above	0.3	0.94	20	0.93	26	0.92	20	0.90	32	0.83	42				
3	2,2'-bis (4,4-dimethyl-2-oxazoline)	0.3	<i>N,N</i> -adipyl biscaprolactam	0.3	1.06	6	1.04	7	1.02	15	1.00	17	0.96	19				
4*	2,2'-bis (2-oxazoline)	0.3	—	—	0.93	8	0.90	12	0.83	20	0.75	30	0.68	46				
Ref.	—	—	—	—	0.78	20	0.76	25	0.74	29	0.72	33	0.70	43				

Table 2

Name of compound	Additive		Properties of extruded polymer													
	Amount added (wt%)	Name of compound	Amount added (wt%)	Residence time 5 min	10 min	15 min	20 min	30 min	( $\eta$ )							
2,2'-bis (2-oxazoline)	0.3	Tetra- <i>n</i> -butyl ammonium bromide	0.01		0.92		0.89	0.83	0.83	0.74	0.74	0.74	0.74	0.67		
Same as above	0.3	Tetrabutyl phosphonium bromide	0.01		0.93		0.88	0.82	0.82	0.73	0.73	0.73	0.73	0.68		
Same as above	0.3	Triphenyl phosphine	0.01	0.91	0.87	0.83	0.72	0.69								
Reaction product of 2-mol of 2,2'-bis (2-oxazoline) and 1-mol of terephthalic acid	1.5	Triphenyl phosphine	0.01	0.81	0.78	0.73	0.69	0.65								

Table 3

Residence time		5	10	15	20	30
( $\eta$ )	1.07	1.03	0.95	0.86	0.71	
(COOH)	6	7	19	40	45	

Table 4

No.	Name of BO compound	Name of BL compound	Properties of extruded polymer								
			Residence time 5 min	10 min	15 min	20 min	30 min				
			( $\eta$ )	(COOH)	( $\eta$ )	(COOH)	( $\eta$ )	(COOH)	( $\eta$ )	(COOH)	
1	2,2'-bis (2-oxazoline) <sup>a</sup>	<i>N,N</i> -terephthalyl biscaprolactam	1.28	6	1.26	7	1.24	10	1.20	13	1.16
2	Same as above	<i>N,N</i> -adipyl biscaprolactam	1.27	7	1.25	7	1.23	11	1.20	13	1.16
3	2,2'-bis (4,4-dimethyl-2-oxazoline)	Same as above	1.29	6	1.26	7	1.25	10	1.19	14	1.15
											16

Figure 1

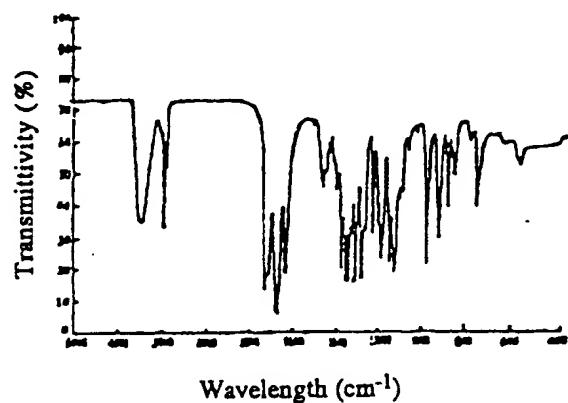


Figure 2

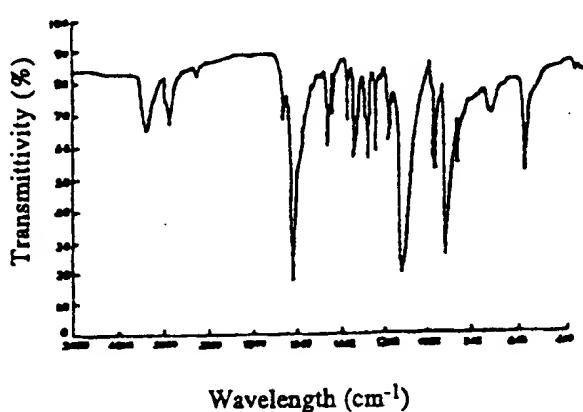
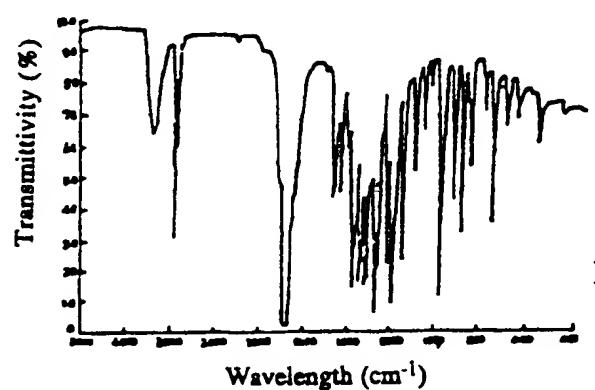


Figure 3



Language Services Unit  
Polyglot International  
November 11, 1994